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Design and Evaluation of a Continuous Flow System with Increased Sample Throughput for Arsenic and Selenium Analysis by ICAP Spectrometry

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AMD Technology Transfer

SUMMARY

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Since 1981, Inductively Coupled Argon Plasma (ICAP) was used for the determination of Arsenic and Selenium in Water, Sediment and Fish. The rate of analysis was 20 samples per hour, using AutoAnalyzer Components, Carlo Erba peristalic pump and a phase separator to channel the hydride gas generated to the (ICAP). Because of the increase of sample number, the method was modified to increase analysis rate from 20 to 40 per hour.

This was achieved by reducing the size of the coil used for stripping hydrides from solution and reducing the dimensions of the gas separator. These modifications improved wash out characteristics (preventing carry over), and also contributes to high sampling rate.

ABSTRACT

The analysis rate for the determination of arsenic and selenium has been increased to 40 per hour from 20 per hour. This is with manual control of the sampler - ICAP interface. When computer control is available the analysis rate can be further increased to 60 samples per hour.

Introduction

An automated system was developed in 1981 to determine arsenic and selenium in environmental samples by Inductively Coupled Argon Plasma (ICAP) (1) (APPENDIX A). This system has been in use in the Water Quality National Laboratories (WQNL) since that time. The sampling rate is 20 samples per hour. The increasing work load of As/Se determinations and other analyses by ICAP have made it desirable to increase the number of samples that can be processed through the ICAP instrument. Studies have been made in NWRI in the past few years on the generation of hydrides from other elements such as lead and tin. There studies have provided some basic reaction-rate data for plumbane and stannane and have, at the same time, given a better insight into the process of generating arsine and hydrogen selenide than was available when the "old" system was developed. With this better understanding a system has been assembled that increases the sample flow rate and decrease the residence time. This results in higher sensitivity and faster wash-out characteristics than with the "old" system.

EXPERIMENT SECTION

Apparatus

The manifold for the system is shown in Figure I. With the exception of the gas separator the equipment used is as previously described (1). The modified gas separator is shown in figure II. The transfer of hydride from the separator to the ICAP torch is now made via 3/16" inch O.D. "Teflon" tubing.

Reagents

There are as previously described with the exception that for each sample an integration time of 30 seconds is used (rather then the 50 seconds previously used).

Method Optimization

The limiting facton in obtaining high flow in a hydride - generation system is the amount of hydrogen produced from the borohydride. As more hydrogen is produced the "noise" in the read-out increases. With larger amounts of hydrogen the plasma is extinguished. At the same time the concentration of borohydride in the total sample flow, among other things, determines how efficently the arenic and selenium are converted to hydrides. In the present work it was shown that, with very rapid mixing and a controlled residence time in the apparatus, the efficiency of the borohydride in producing hydrides is increased. Thus it is possible, relative to the "old" system (1), to approximately double the sample flow and obtain twice the amount of hydride while maintaining the same borohydride flow, (and hence hydrogen production).

Reducing the size of the coil used for stripping hydrides from solution and reducing the dimensions of the gas separtor give improved wash-out characteristics and this also contribrates to a high sampling rate.

The system is presently operated with a manual interface between the sampler and the ICAP read-out. The integration starting time is triggered by depressing a key on the control keyboard. Because of the uncertainties involved in this operation the system is run at 40 samples per hour, with a one minute sample, a 30 second wash, and a 30 second integration time.

When the sampler and read-out are interface via the instrument computer the rate can be increased to 60 samples per hour. This will use a 45 second sample, a 15 second wash and a 30 record integration period.

A phenomenon with the continuous-flow system that we have observed is that, at the beginning of each selenium peak a small "spike" occurs. Integration of the peak is delayed until this spike has passed. The spike is believed to be due to the fact that some hydrogen selenide from the sample decomposes in the hot torch and is deposited on the end of the injector top. This material is then volatilized at the beginning of the next sample by the air bubble that is taken in as the sampler arm moves from the wash receptacle to the sample tube. It can be avoided by adding a continuous small air bleed to the system and this is done by using a pump tube in the manifold.

Precision and Detection Limits

The precision of the determination was measured at the 1 ug L^{-1} and the 10 ug L^{-1} level in the sample flow. (Since for water analysis a five-fold pre-concentration is used these levels correspond to 0.2 ug L^{-1} and 2 ug L^{-1} respectively in the water sample). The relative standard deviation obtained were 3.5% and 2.1% for As are Se at the 1 ugL^{-1} level and 1.4% and 1.7% for As and Se at the 10 ugL^{-1} level. There determinations were made both by replicating each level directly and by alternating the 1 are 10 ugL^{-1} standards. There was no signficant difference between the two mode of operation.

The detection limits for water samples, with the five-fold pre-concentration were 0.006 ug L^{-1} for As and 0.02 ug L^{-1} for Se (these were calculated as described (1)).

Analysis of Samples

Forty water samples and forty-three fish samples were analysed with the "old" method (at 20 per hour) and the present method (at 40 per hour). These results are shown in Tables I and II.

In the 40 water samples the mean difference for selenium values was .02 ug L^{-1}, in the 20 water samples where the arsenic values were below 1 ug L^{-1} the mean difference was 0.04 ug L^{-1}. These differences are statistically significant but are believed not to be of physical significance. In the 43 fish samples there was no difference in the mean values in the arsenic determination, in the selenium values the mean difference was .006 ug g^{-1}.

The results obtained from standard reference materials and the recoveries obtained from spiking samples are shown in Table III.

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TABLE I - ANALYSIS OF WATER SAMPLES

LAB NO.	OLD AS ug/L	NEW AS ug/L	OLD SE ug/L	NEW SE ug/L
15760	0.68	0.68	1.15	1.24
15761	0.62	0.60	1.08	1.17
15762	0.61	0.61	1.12	1.19
15763	0.62	0.60	1.11	1.18
15764	0.77	0.72	1.43	1.50
15765	31.0	30.9	0.16	0.12
15766	32.5	31.9	0.14	0.10
15767	35.4	35.4	0.13	0.04
15768	39.9	40.4	0.15	0.10
15769	34.4	34.2	0.11	0.05
15770	0.41	0.39	0.10	0.12
15771	0.32	0.31	0.04	0.10
15772	0.35	0.29	0.06	0.03
15773	0.32	0.30	0.02	0.05
15774	0.44	0.42	0.08	0.07
15775	2.66	2.50	0.35	0.43
15776	3.06	2.83	0.36	0.43
15777	3.02	2.85	0.25	0.30
15778	2.86	2.69	0.37	0.47
15779	2.92	2.67	0.37	0.47
15780	3.00	2.85	0.48	0.48
15781	3.09	2.95	0.45	0.47
15782	3.15	2.91	0.45	0.46
15783	3.16	2.93	0.45	0.47
15784	3.09	2.87	0.49	0.47
15785	0.64	0.59	0.26	0.26
15786	0.53	0.52	0.23	0.27
15787	0.54	0.48	0.27	0.27
15788	0.56	0.49	0.25	0.27
15789	0.58	0.54	0.33	0.29
15790	1.21	1.11	0.22	0.17
15791	1.26	1.17	0.94	1.09
15792	1.25	1.13	0.21	0.19
15793	1.23	1.13	0.18	0.18
15794	1.18	1.11	0.15	0.15
15795	0.69	0.69	0.14	0.15
15796	0.69	0.69	0.11	0.13
15797	0.68	0.64	0.11	0.14
15798	0.70	0.66	0.14	0.16
15799	0.70	0.63	0.09	0.14

TABLE II - ANALYSIS OF FISH SAMPLES

LAB NO.	AS		SE	
	20 SAMP/HR ug/g	40 SAMP/HR ug/g	20 SAMP/HR ug/g	40 SAMP/HR ug/g
8302631	.32	.33	.35	.34
02738	.12	.11	.61	.62
02739	.09	.09	.66	.65
02740	.11	.11	.55	.54
02741	.08	.10	.61	.63
02745	.10	.12	.58	.55
02746	.05	.07	.56	.57
02747	.12	.14	.55	.53
02750	.10	.11	.40	.38
02751	.19	.20	.56	.50
02752	.05	.07	.43	.41
02754	.09	.11	.43	.41
02755	.07	.07	.40	.35
02757	.11	.15	.37	.38
02758	.16	.18	.36	.35
02760	.09	.22	.44	.43
02761	.08	.09	.39	.39
02762	.17	.18	.38	.38
02763	.14	.14	.39	.39
02766	.08	.10	.40	.40
02767	.10	.12	.39	.39
02769	.10	.10	.44	.43
02770	.14	.12	.46	.45
02771	.12	.11	.46	.44
02772	.16	.16	.53	.52
02773	.12	.10	.46	.44
02774	.15	.14	.46	.44
16717	.12	.11	.32	.33
16721	.08	.06	.22	.23
16722	.12	.10	.20	.22
16723	.10	.07	.25	.25
16724	.09	.07	.21	.21
16725	.12	.10	.29	.30
16726	.18	.15	.29	.29
17365	.08	.08	.91	.95
17366	.09	.09	.93	.96
17367	.07	.07	.79	.81
17368	.08	.07	.61	.58
17369	.11	.11	.91	.92
17370	.07	.06	.88	.88
17371	.06	.06	.70	.70
17372	.09	.09	.68	.68
17373	.74	.74	.47	.45
n =	43	43	48	48
MEAN =	.13	.13	.48	.48
STD =	.11	.11	.19	.19

TABLE III - ANALYSIS OF REFERENCE MATERIALS

AND SPIKE RECOVERY WITH SAMPLES

REF	AS		SE	
	20 SAMP/HR ug/g	40 SAMP/HR ug/g	20 SAMP/HR ug/g	40 SAMP/HR ug/g
OYSTER TISSUE	12.1	13.0	2.1	2.0
	(13.4 +/- 1.9)		(12.1 +/- 0.5)	
ALBACORE TUNA	2.78	2.96	3.38	3.26
	(3.3 +/- 0.4)		(3.6 +/- 0.4)	
LOBSTER TISSUE	24.4	26.8	5.69	5.76
	26.5	26.1	5.58	5.63
	(24.6 +/- 2.2)		(6.88 +/- 0.47)	
	SPIKE RECOVERY			
LAB NO.				
02761	0.08	0.09	0.39	0.39
	0.28	0.29	0.58	0.58
	100%	100%	95%	95%
16717	0.12	0.11	0.32	0.33
	0.34	0.32	0.53	0.49
	110%	105%	105%	80%
16724	0.09	0.07	0.21	0.21
	0.30	0.28	0.41	0.41
	105%	105%	100%	100%
17373	0.74	0.74	0.47	0.45
	0.94	0.92	0.65	0.65
	100%	90%	90%	100%

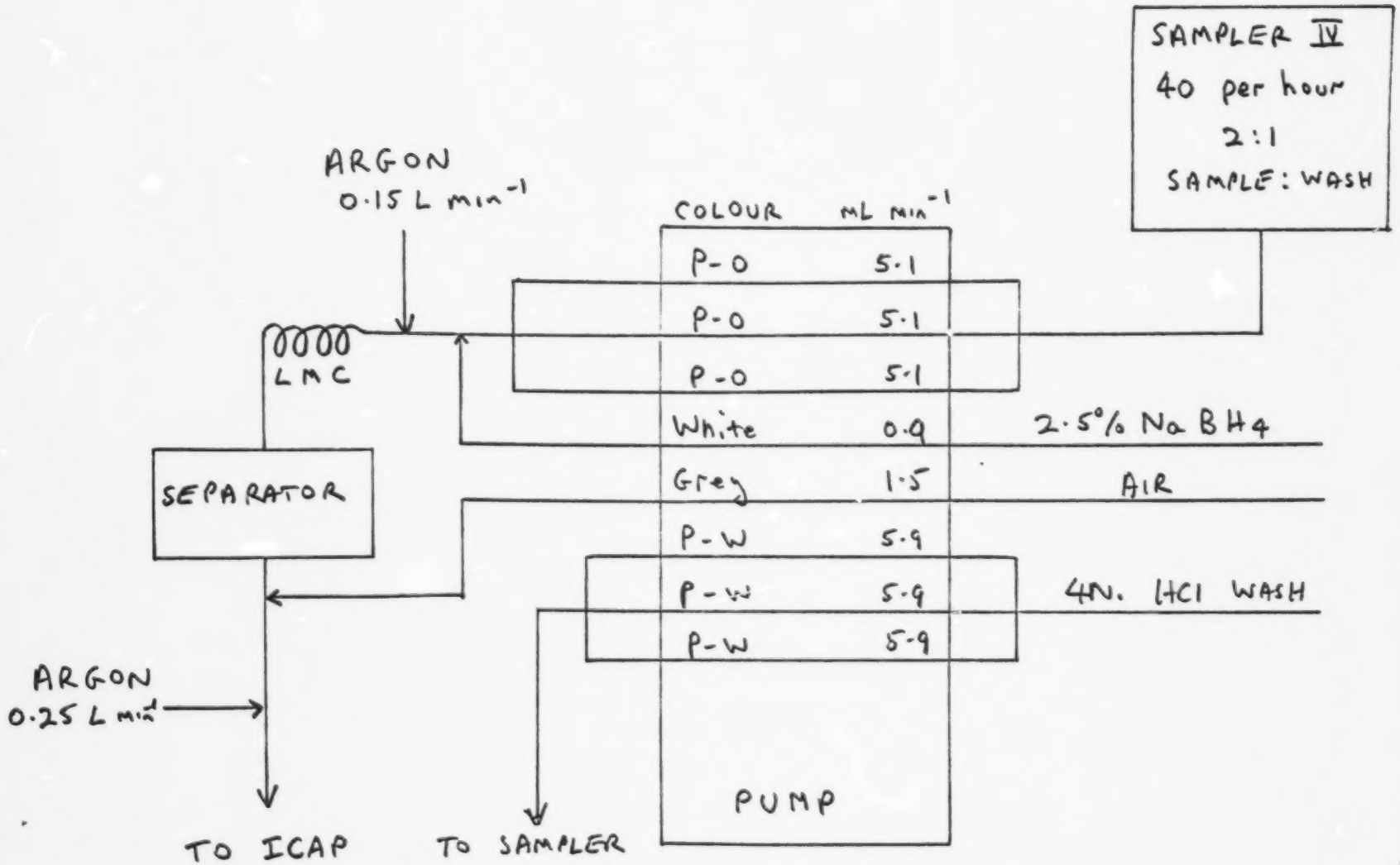

FIGURE I - MANIFOLD

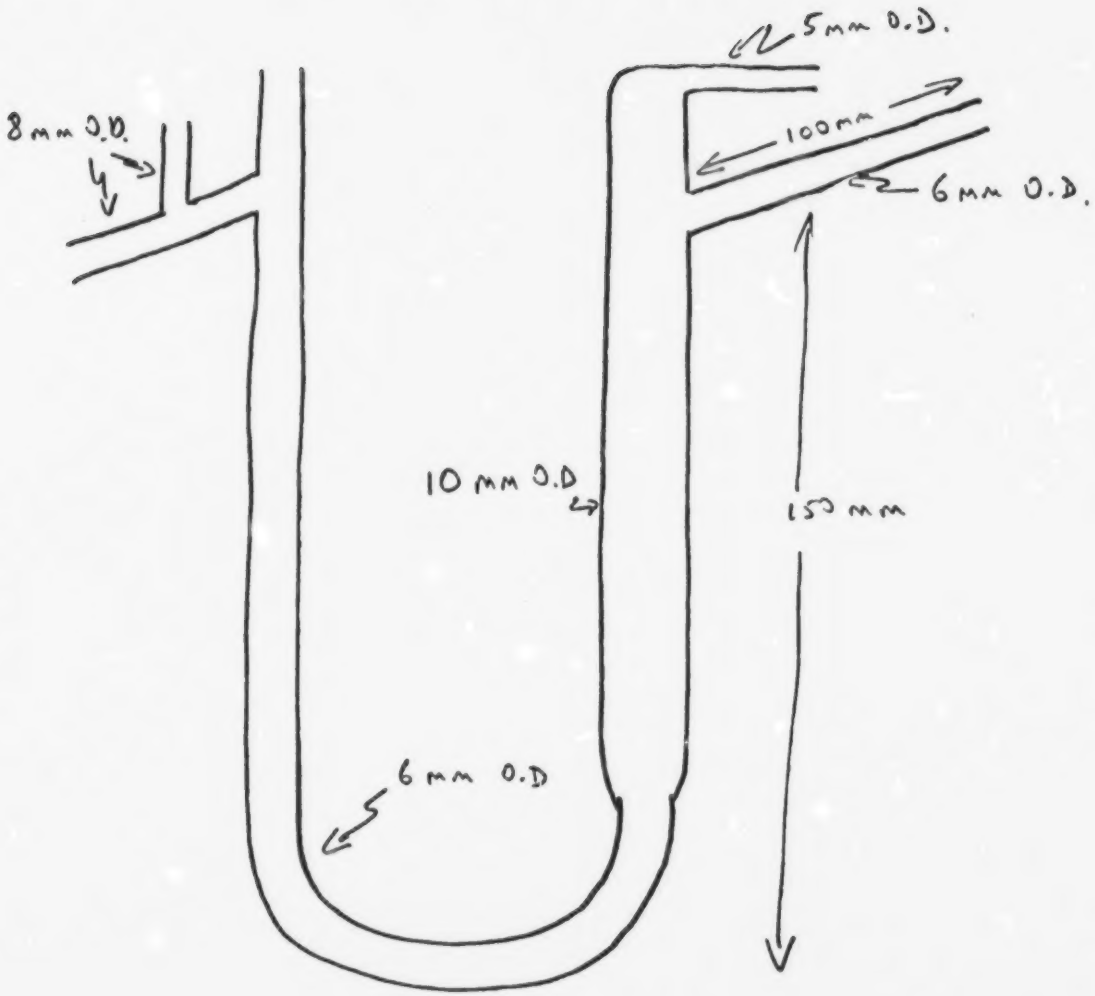

FIGURE II · SEPARATOR

APPENDIX 'A'

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Determination of Arsenic and Selenium in Water, Fish, and Sediments by Inductively Coupled Argon Plasma Emission Spectrometry

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A semiautomated system for the determination of As and Se by hydride generation is described. By use of a preconcentration step (×4) for water, detection limits are 0.02 and 0.03 $\mu g\ L^{-1}$ for As and Se, respectively. Fish are digested with nitric, perchloric, and sulfuric acids; sediments are brought into solution by fusion with sodium hydroxide. The automated measurement system uses conventional continuous flow equipment connected to a "larger-diameter-than-usual" torch in the inductively coupled argon plasma (ICAP) instrument.

Arsenic and selenium levels in environmental samples (i.e., water, fish, and sediment) are currently determined in this laboratory using a continuous flow hydride generating system and atomic absorption spectrometry (*1*). The use of atomic emission spectrometry with inductively coupled argon plasma excitation (ICAP) offers an alternative route to these determinations. In addition, ICAP provides the opportunity to simultaneously determine the other hydride-forming elements of interest to us, namely, tin, antimony, and bismuth. There have been many analytical systems developed to carry out these determinations, in particular the system described by Thompson et al. (*2*) will simultaneously determine As, Sb, Bi, Se, and Te in an automated system. However, this system is not completely suitable for our needs in that it does not use a conventional continuous flow system, it uses a higher power

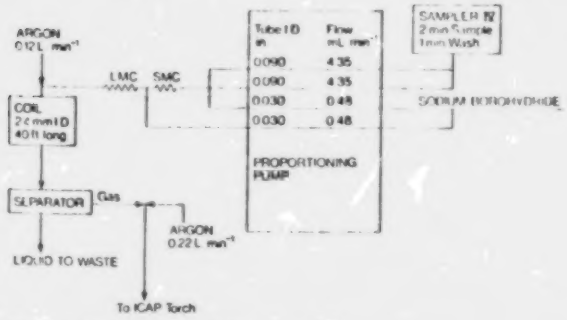

Figure 1. Manifold for hydride generation.

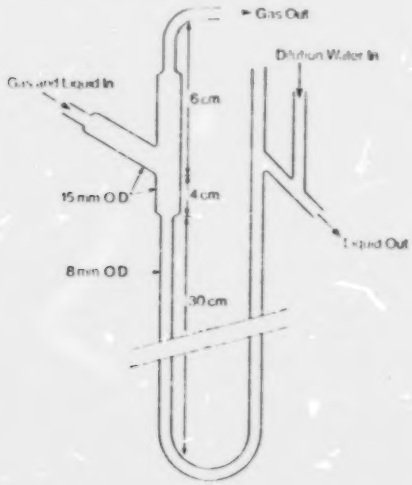

Figure 2. Gas separator.

(2500 W) in the rf system than is commonly available, and determination of selenium in sediments requires a separate treatment process. In the work described here, conventional continuous flow equipment is used with a plasma power of 1400 W. The detection limits obtained for water (with a preconcentration step) are 0.03 $\mu g\ L^{-1}$ for Se and 0.02 $\mu g\ L^{-1}$ for As. Sediments are brought into solution by fusion with NaOH in a zirconium crucible.

EXPERIMENTAL SECTION

Apparatus. The manifold used for the automated hydride generation is shown in Figure 1. The sampler is a Sampler IV (Technicon Corp.) with the tray modified to use 18 × 150 mm sample tubes. The pump is a 20-channel proportioning pump (Carlo Erba) [a Pump III (Technicon Corp.) has also been found satisfactory]. Details of the gas separator are shown in Figure 2. This equipment is located in a fume hood and the gas conveyed to the ICAP via 2 m of 3 mm i.d. glass tubing.

The ICAP system is an Applied Research Laboratory ICP torch compartment with a Model No. QA-137 spectrometer. The spectrometer has a grating having 1080 lines mm^{-1} blazed at 600 nm with the measurements being made in the third order. The measurements are made at 193.76, 203.99, 223.06, 206.83, and 189.99 nm, respectively, for arsenic, selenium, bismuth, antimony, and tin. The instrument has been modified to fit the spectrometer enclosure with a temperature control system that maintains the enclosure at 30 ± 0.2 °C and to provide the matching network components with water cooling.

The torch body is made from standard wall silica tubing as shown in Figure 3. The sample gas stream is added to the plasma through silica tubing having 3 mm bore with a 10 mm length of 2 mm bore capillary tube attached to its upper end. This is inserted up the middle of the 5 mm i.d. tube at the center of the torch body.

The crucibles used for the alkaline fusions are 15-mL zirconium crucibles.

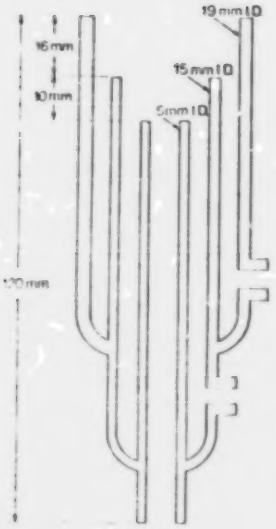

Figure 3. Torch body.

Reagents. The potassium persulfate solution is made by dissolving 4 g of potassium persulfate in 100 mL of water. The sodium borohydride solution is made by dissolving 2.5 g of sodium borohydride in 100 mL of 0.5 N NaOH solution. The wash solution used in the automated system is made by adding one volume of hydrochloric acid to two volumes of water.

Procedure. *Sample Pretreatment.* Water samples are pretreated in the following way. To a 100-mL sample in a 250-mL conical flask is added 7 mL of potassium persulfate solution and 3 mL of hydrochloric acid. The flask is placed on a shaker hot plate and the solution evaporated to approximately 10 mL volume. The flask is cooled and the concentrated sample transferred to a 25-mL graduated cylinder, where the volume is made to 15 mL with water and 6 mL of hydrochloric acid is added. The sample is returned to the flask and heated to maintain the temperature above 90 °C for 20–30 min (to convert the selenate to selenite). The sample is cooled and transferred to the sampler tube for analysis. The standard solutions for calibration are treated similarly.

Sediment samples are pretreated in the following way: 2 g of solid NaOH is placed in a zirconium crucible and 0.2 g of the dried ground sediment is added. The crucible is placed in a cold furnace which is then heated to 350 °C for 2 h. The crucible is cooled and the contents are dissolved in 40 mL of 0.2 N hydrochloric acid. Twenty milliliters of hydrochloric acid is then added and the solution heated to about 90 °C for 1 h. The precipitated silicic acid is allowed to settle and the solution decanted into the sampler tubes. A calibration curve is obtained by using standard solutions of As and Se in 4 N hydrochloric acid. Fish samples are treated by the procedure of Agemian and Thomson (3).

ICAP Determination. The automated system is started by using water in place of the sodium borohydride reagent. The plasma is ignited and allowed to operate for about 45 min as a warmup period. The borohydride flow is then started, first through one pump tube and after a few minutes through both pump tubes. (The two-stage addition allows time to "tune" the plasma when the hydrogen generation starts.) The operating parameters for the ICAP are as follows: forward power, 1400 W; reflected power, less than 10 W; cooling gas flow, 12 L min^{-1}; plasma gas flow, 0.12 L min^{-1}; injector flow, 0.34 L min^{-1}. Each sample is aspirated for 2 min with a 1-min wash. Five 10-s integrations are made with each sample and standard.

RESULTS AND DISCUSSION

Method Optimization. The fraction of the arsenic and selenium that is converted to the hydride is, among other parameters, a function of the borohydride concentration in the reaction solution. This relationship is shown by Thompson et al. and was confirmed in the present work. The stripping of the hydrides from the solution into the gas stream was

Table I. Results on Reference Soils and Sediment

	As content, $\mu g\ g^{-1}$		Se content, $\mu g\ g^{-1}$	
sample[b]	recommended level	present method	recommended level	present method
SO-1	1.9	1.9	0.1	0.09
SO-2	1.2	1.3	0.3	0.31
SO-3	2.6	2.6	0.05	0.08
SO-4	7.1	6.5	0.4	0.49
I.A.E.A. (soil 5)	93.9 ± 7.5[a]	95.1		0.93
N.B.S. (S.R.M. 1645)	66	66.4		1.0

[a] Certified value. [b] SO, reference soils from Canada Centre for Mineral & Energy Technology; N.B.S., National Bureau of Standards, U.S.A.; I.A.E.A., International Atomic Energy Agency, Vienna, Austria.

studied and a variety of stripping devices, such as the heated packed columns used in previous work (*1*), were investigated. It was found that, with the large volume of hydrogen generated in the reaction and the large volume of argon used in the plasma, essentially all of the hydride could be transferred to the gas phase using the unheated glass coil shown. The gas that carries the hydride into the plasma must be at a rate sufficient to "punch" a hole into the middle of the plasma: below this rate the sample bypasses the center of the plasma, above this rate the signal is reduced because of dilution of the sample stream. It was found that if all the gas was added before the stripping coil, the gas became saturated with water and there were problems with condensation in the long tube leading to the torch. By addition of some of the argon after the liquid had separated, this problem of condensation was avoided.

It was also found advantageous to make changes to the "standard" torch. The torch used for most ICAP applications has an outer tube of 17 mm i.d. When hydrogen is introduced the plasma narrows down and the signal becomes much noisier. The noise was attributed to the problem of uneven sample addition at the bottom of the plasma. When the diameter of the outside tube was increased to 19 mm, the plasma, when connected to the hydride generator, had the same shape and noise characteristics of a "normal" plasma operating in a 17-mm tube. The auxilliary tube was also increased in size (as shown in Figure 3) to maintain approximately the same annular space for the cooling flow. The sample addition tube is the most vulnerable part of the torch, it erodes quite quickly and it was found that after a few weeks of operation the torch would become unserviceable because of this. The demountable sample tube is used so that it can be removed and the end reground or the tube replaced. The diameter of this tube at the addition point was varied and it was found that there was little effect on the signal and noise characteristics as the diameter was changed over the range 0.7–2.5 mm. At the larger diameters, however, there was less back-pressure on the liquid–gas separator and the 2 mm diameter was selected as a convenient size.

The system gives very stable operation. The flow paths of the liquid and gas are sufficiently long that there is no effect on the plasma from the pulsations of the pump and the air bubble that is taken in at the beginning and end of each sample passes through the plasma with no difficulty.

Detection Limits. The detection limits depend on the sensitivity and the noise of the analytical system. The noise can be considered to be made up of two parts, the short-term noise, such as is seen in 10 consective 10-s integrations, and the long-term changes over the analytical day. Before the temperature control system was installed on the spectrometer and matching network, it was found that typically the long-term changes would be from 10 to 20 times those of the short-term noise. After the installation of the temperature control systems these long-term variations disappeared. To monitor these changes, ten consecutive 10-s integrations at the zero level were taken every 15 min during several analytical runs of about 5 h each. Analysis of variance of these data typically showed that after the first 45 min of operation there was no statistical difference "between" the 10 consecutive integrations compared to the variance "within" the 10 integrations. Hence, all of these results at the zero level can be used to determine the noise of the system. These results gave standard deviation corresponding to 0.03 $\mu g\ L^{-1}$ Se and 0.02 $\mu g\ L^{-1}$ As in a water sample. Since each sample is replicated five times, these values are the theoretical detection limits for the analysis. In practical terms it is possible to reliably report values down to 0.1 $\mu g\ L^{-1}$ for each element (this is the current practice with the automated hydride, atomic absorption analytical system).

It should be noted that the same precision and sensitivity are achieved by using a single 50-s integration. We have, however, chosen to use five 10-s integrations and to have calculated and printed out the mean and standard deviation for each of the samples, standards, and blanks. This provides a continuing check on the stability of the analytical system.

Water Analysis Fish Analyses. A comparison of results on typical natural waters and on fish samples showed no significant differences between them and the results by the hydride generation, atomic absorption technique.

Sediment Analysis. Analysis of six reference soil and sediment samples gave results for As and Se that were acceptable. These results are shown in Table I. A study of the interferences from other elements in sediment samples has been made by Thompson et al. (*4*). Their conclusions were that a separation from interfering elements was necessary and they used a lanthanum hydroxide precipitation to achieve this. With the higher dilutions used in the present method it was decided that such a separation is not necessary for the sediment samples that we analyze. To monitor the validity of the decision representative sediments were analyzed and standard additions of As and Se were made in the fusion step and also to the solutions of the fusion mixes. The slopes of the calibration lines obtained with both of these types of standard additions were the same as those obtained in a water matrix. The elemental composition of the fusion solutions can easily be determined by ICAP and the data of Thompson et al. (*4*) used to determine if interferences are a problem and whether a separation step is necessary or if compensation can be made in the software program for the calculation of ICAP results. (The programming to make corrections for interferences such as this is part of the software package supplied with the instrument.)

Other Elements. The other hydride forming elements, such as Sb, Sn, and Bi, have been determined in water simultaneously with As and Se. (It is recognized that the 4 N acid used in the method is not the optimum for stannane production and that somewhat less than 10% of the potential stannane is produced.) The detection limits obtained are 0.02, 0.05, and 0.03 $\mu g\ L^{-1}$ for Sb, Sn, and Bi, respectively. At the present time these elements have not been determined in fish or sediment using our method.

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